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SYNTHESIS OF HIGH-NITROGEN CONTENT HETEROCYCLIC NITRAMINES AND ENERGETIC INTERNAL PLASTICIZERS

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Rodney L. Willer, Ph.D.
Morton Thiokol, Inc.
Elkton Division
Elkton, Maryland 21921

JUNE 1987

FINAL REPORT FOR FEBRUARY 1985-MARCH 1987

Approved for Public Release

Prepared for
AIR FORCE OFFICE OF SCIENTIFIC RESEARCH
Directorate of Chemical and Atmospheric Sciences
Building 410
Bolling Air Force Base, DC 20332-6448

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19. ABSTRACT (Continue on reverse if necessary and identify by block number)

The synthesis of several novel high-nitrogen content heterocyclic compounds and their nitramine derivatives is described. The compounds are highly energetic and frequently have higher calculated performance as a mono propellant than RDX or HMX.

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In reply refer to: E116-87

June 24, 1987

Dr. Anthony Matuszko
Air Force Office of Scientific Research
Directorate of Chemical and Atmospheric Sciences
Building 410
Bolling Air Force Base, DC 20332-6448

Subject: Final Technical Report

Reference: Contract F49620-85-C-0036

Gentlemen:

In accordance with Item 0002AA of the reference contract, enclosed are 16 copies of the final technical report, E116-87, on our work on the synthesis of high-nitrogen content heterocyclic nitramines and energetic internal plasticizers. This basic research program was started in February 1985 and was completed in March 1987.

If you have any questions, please contact Dr. R. L. Willer or the undersigned.

Very truly yours,

E C Oosterom

E. C. Oosterom
Program Manager
Advanced Technology Department

Approved for public release; distribution unlimited.

ECO/py
Enclosure: E116-87 (16 copies)

cc: Ms. Louise Harrison
Chief, Support Services Department
Directorate of Contracts
Department of the Air Force
Air Force Office of Scientific Research
Bolling Air Force Base, DC 20332-6448

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E116-87

MORTON THIOKOL, INC.
ELKTON DIVISION
ELKTON, MARYLAND

SYNTHESIS OF HIGH-NITROGEN CONTENT HETEROCYCLIC NITRAMINES AND ENERGETIC INTERNAL PLASTICIZERS

FINAL REPORT

PREPARED FOR
AIR FORCE OFFICE OF SCIENTIFIC RESEARCH
BOLLING AIR FORCE BASE, DC

June 1987

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Ernest S. Sutton

Ernest S. Sutton
Vice President and General Manager

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1.0 INTRODUCTION

This report will summarize the work accomplished by the Elkton Division of Morton Thiokol, Inc., under an Air Force Office of Scientific Research (AFOSR) sponsored program entitled, "Synthesis of High Nitrogen Content Heterocyclic Nitramines and Energetic Internal Plasticizers" (Contract No. F49620-85-C-0036). The principle investigator at Morton Thiokol/Elkton was Dr. Rodney L. Willer. He was assisted by Mr. Richard Biddle, who determined the heats of combustions and differential scanning calometry, and Dr. Glen Cunkle (synthesis). The program was initiated in March 1985 and concluded in March 1987. Dr. Anthony Matuszko was the program manager at AFOSR.

2.0 OBJECTIVES

The objectives of this program were to: 1) investigate the synthesis of compounds with furazan, furoxan, and tetrazole rings fused to saturated heterocyclic rings such as piperazine, hexahydropyrimidine, hexahydrotriazine, tetrazocine and the nitramine derivatives of these compounds, and 2) conduct basic research on internal plasticizers (IP) and energetic internal plasticizer (EIPs) so as to develop design criteria for IPs and EIPs for various polymer systems. This should allow combining the advantages of EIP and energetic polymers so as to optimize the energy and mechanical properties of propellant binder systems.

3.0 APPROACH AND ACCOMPLISHMENTS

This section is divided into three sections covering the work accomplished on 1) the synthesis and chemistry of furazan and furoxan fused compounds 2) synthesis and chemistry of tetrazole fused compounds, and 3) internal plasticizers and energetic internal plasticizers.

3.1 Summary of Accomplishments

1. Based on measured heats of formation for furazans and furoxans, there appear to be no thermochemical reasons why furazans have not been successfully oxidized to furoxans.

2. The lower barrier to isomerization of benzofuroxans as compared to dialkyl furoxans is reasonable in view of the larger diference in the heats of formations of benzofurazan and benzofuroxan as compared to the heats of formations of dialkyl furazans and dialkyl furoxans.

3. Attempts to synthesize dinitrodifurazanodiazopine and dinitrohexahydrofurazano-pyrimidine were unsuccessful.

4. Methylene bis (3-nitramino-4-methylfurazan) was synthesized by the condensation of 3-amino-4-methyl furazan with formaldehyde and subsequent nitration of this product.

5. One aminotetrazole was condensed with formaldehyde to give in low yield methylene bis(1-aminotetrazole).

6. 5,6-dihydro-7H-imidazolo [1,2-d] tetrazole was nitrated to 5-nitro-5,6-dihydro-7H-imidazolo [1,2-d] tetrazole. This compound definitely has the tetrazole structure as shown by x-ray crystallography.

7. 1,5-diaminotetrazole condenses with glyoxal and substituted glyoxals to give tetrazolotriazines when a 1:1 stoichiometry is used and hexaazadecalin analogs when a 2:1 stoichiometry is used.

8. The tetrazolo-as-triazines can be reduced to dihydro and tetrahydro-derivatives by hydrogenation (Pd/C calalyst) and tetrahydro derivatives by sodium borohydride in methanol.

9. The tetrahydrotetrazolotriazines can be nitrated to the dinitro derivatives while the dihydro compounds only nitrate to a mononitro compound.

3.2 Synthesis and Chemistry of Furazan and Furoxan Fused Compounds

3.2.1 Heats of Combustions and Heats of Formations of α-Dioximes, Furazans, and Furoxans. Furazans (1,2,5-oxadiazoles) and furoxans (1,2,5-oxadiazole-2-oxides) are related rings systems with a furoxan being the N-oxide of a furazan (see Figure 1).

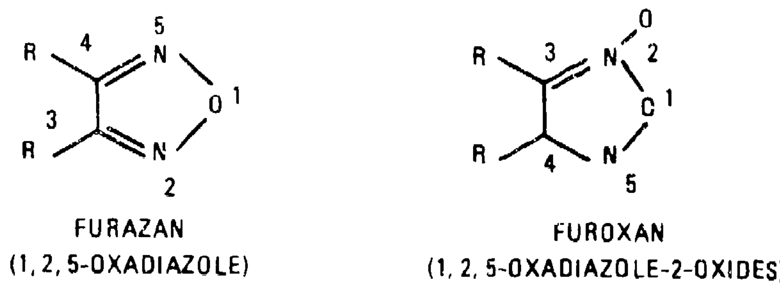
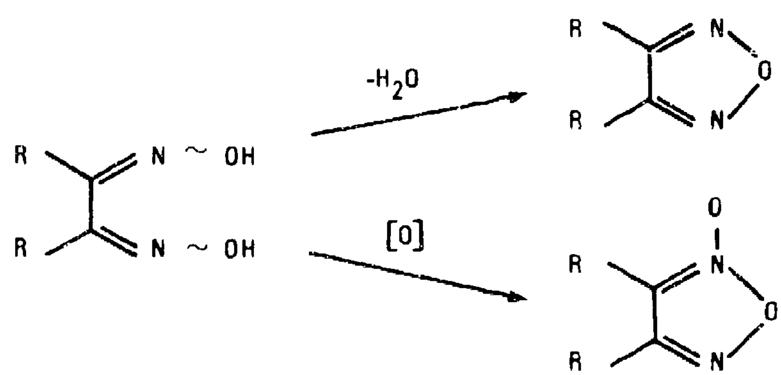
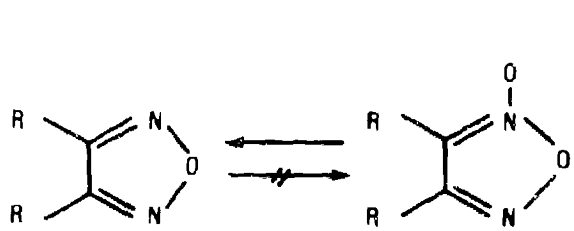


Figure 1. Structure of Furazan and Furoxan Ring Systems

Both ring systems are conveniently prepared from α-dioximes, the furazans by dehydration and the furoxans by oxidation.[1] One of the curious aspects of furazan and furoxan chemistry is that the reduction of furoxans to furazans is a well established reaction, while the oxidation of a furazan to a furoxan is an unknown reaction (see Scheme 2).



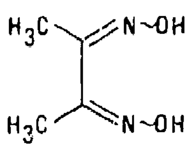
Scheme 1. Synthesis of Furazans and Furoxans from α-Dioximes



Scheme 2. Interconversions of Furazans and Furoxans

This is in contrast to other heterocyclic systems such as pyridine where oxidation and reduction are both well established. It would be desirable to be able to oxidize furazans to furoxanes because the greater oxygen balance of furoxans make them more energetic. Therefore, a study of the heats of combustions and heats of formation of a number of α-dioximes, furazans, and fuorxans was conducted to gain some insight into this problem. The compounds whose heats of combustion were determined are shown in Figure 2 and the measured heats of combustion and calculated heats of formation are summarized in Table 1. The compounds were purchased or synthesized according to published literature procedures and purified by recrystallization to a constant melting point or decomposition temperature. The references to the syntheses of the compounds are **2**[3], **3**[4], **4** - **6**[5], **7** - **8**[6], **10**[7], **11**[8], and **12** - **13**[5]. The heat of formation data in Table 1 have been rearranged in Table 2 and the differences in the heats of formation of the α-dioximes, and the furazans and furoxans are summarized.

The measured heat of formation of dimethylglyoxime is consistent with the known heat of formation of glyoxime (-21.1 kcal/mole) and tetramethylene glyoxime (-81.6 kcal/mole).[10] The rest of the values appear reasonable except perhaps the values for compounds **4**, **5**, and **6** where the value for **4** appears low compared to that obtained for compounds **10** and **12**. In reality, this data shed little light on the reason(s) why furazan cannot be oxidized to furoxans. The data for dimethylglyoxime, dimethyl furoxan, o-benzoquinone dioxime, and benzofuroxan do shed some light on the reason for the large difference in the barrier to isomerization (see scheme 3) in dimethyl furoxan and benzofuraxan (34 kcal/mole vs 14 kcal mole). The larger difference between the heats of formation of benzofurazan and benzofuroxan than between dimethylfurazan and dimethylfuroxan (16.4 vs 3.1 kcal/mole) would support a much larger contribution of the vinyl dinitroso structure in the benzo case. This is reasonable since one gains the resonance stabilization of the benzene ring in this structure.



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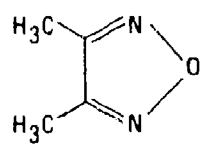

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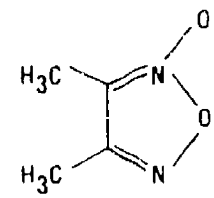

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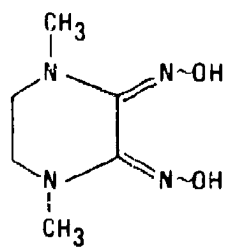

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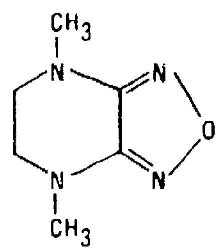

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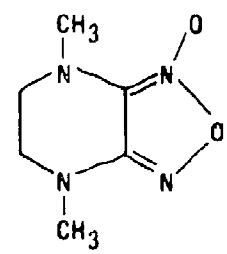

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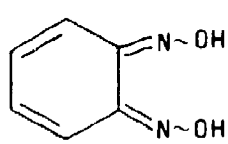

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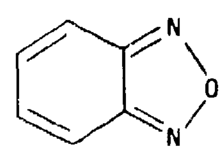

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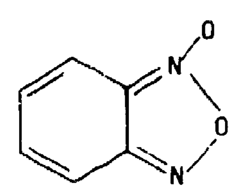

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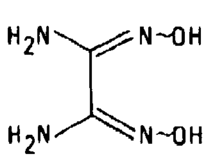

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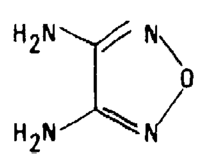

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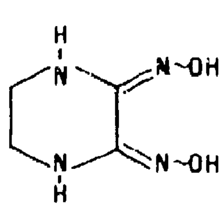

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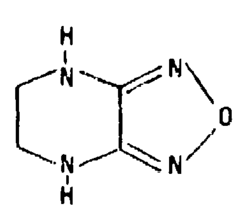

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Figure 2. Compounds Studied

TABLE 1. Summary of ΔH_f's

Compound	Molecular Formula	Molecular Weight	ΔH_c, cal/g	ΔH_f, kcal/mole
1	$C_4H_8N_2O_2$	116.124	5204 ±53	-45.4 ±0.5
2	$C_4H_6N_2O$	98.108	6040 ±12	+11.2 ±0.1
3	$C_4H_6N_2O_2$	114.108	5166 ±17	8.1 ±0.1
4	$C_6H_{12}N_4O_2$	172.184	5348 ±23	-53.7 ±4.0
5	$C_6H_{10}N_4O$	154.168	5976 ±112	+15.1 ±17.3
6	$C_6H_{10}N_4O_2$	170.168	5389 ±109	+10.9 ±18.6
7	$C_6H_6N_2O_2$	138.122	5587 ±	+2.3 ±
8	$C_6H_4N_2O$	120.106	6326 ±	+58.8 ±
9	$C_6H_4N_2O_2$	136.106	5463 ±	+42.9 ±
10	$C_2H_6N_4O_2$	118.096	3024 ±13	-36.0 ±1.5
11	$C_2H_4N_4O$	100.080	3417 ±4	+17.2 ±0.4
12	$C_4H_8N_4O_2$	144.132	4323 ±2	-26.7 ±0.3
13	$C_4H_6N_4O$	126.116	4820 ±7	+26.5 ±0.9

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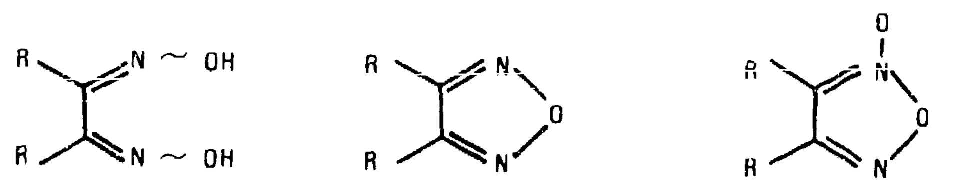
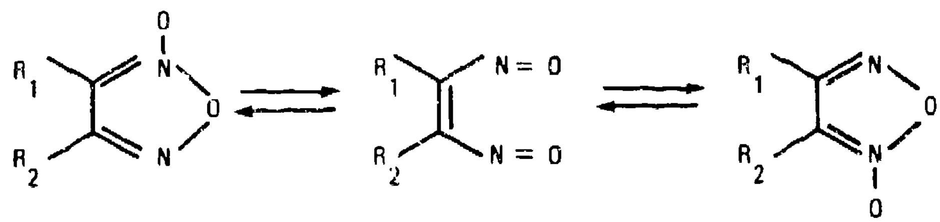
TABLE 2. Heats of Formation of Selected α-Dioximes, Furazans and Furoxans



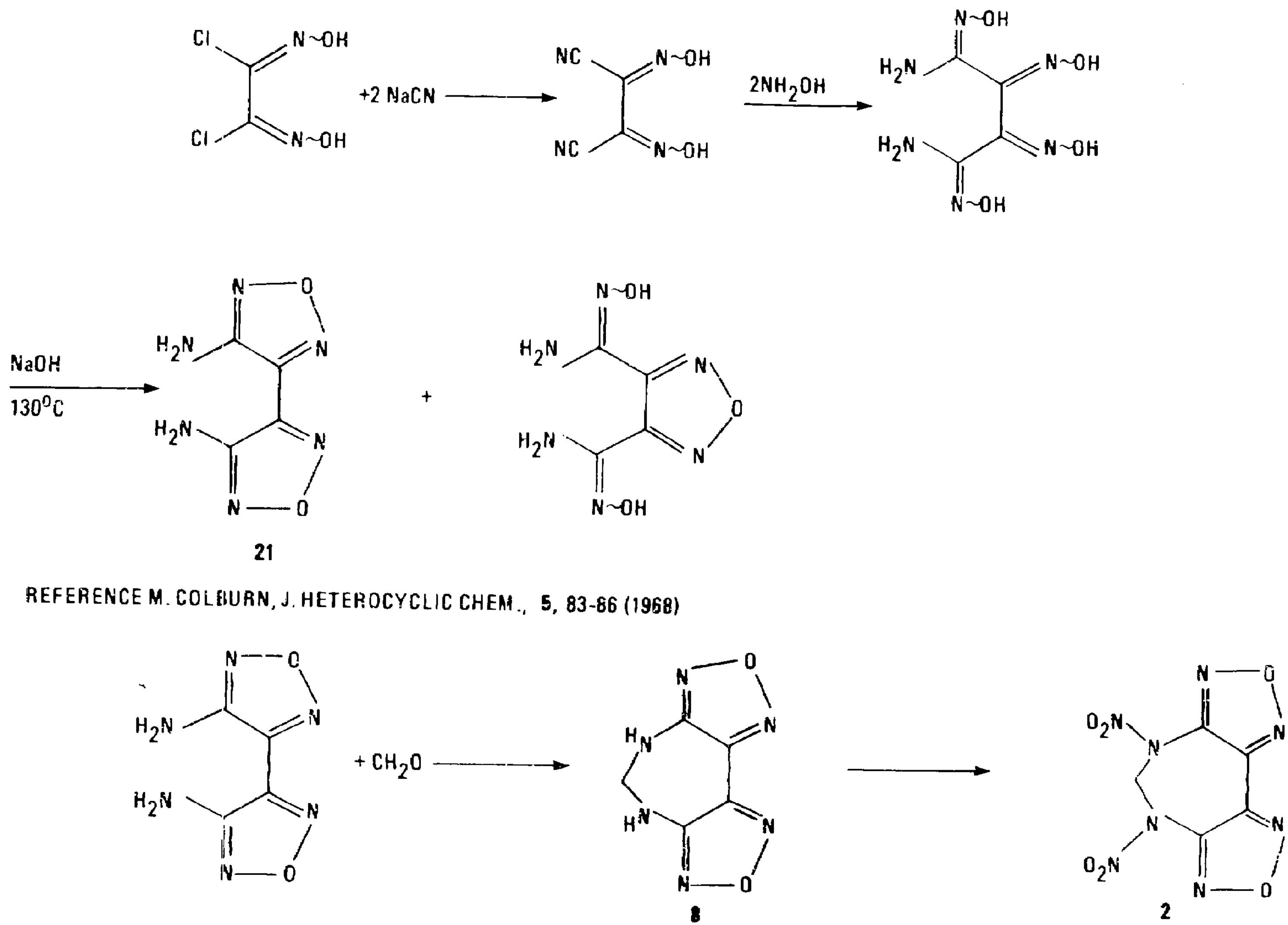
R	R′	ΔHf	ΔHf	Δ(ΔHf)	ΔHf	Δ(ΔHf)
CH_3	CH_3	-45.4	+11.21	56.6	+8.1	53.5
$CH_3NCH_2CH_2NCH_3$		-53.7	+15.1	68.8	+10.9	64.6
BENZO		+2.3	+58.8	56.5	+42.4	40.1
NH_2	NH_2	-36.0	+17.2	53.2	–	
$HNCH_2CH_2NH$		-26.7	+26.5	53.2	–	



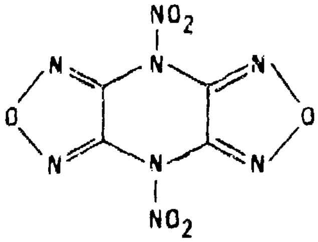
Scheme 3. Isomerization of Furoxans

3.2.2 Synthesis of Furazano and Furoxano Fused Saturated Heterocycles. Figure 3 shows the structures of the furazans and furoxans which were selected as target molecules. During this project, synthetic efforts have concentrated on compounds **15**, **16**, and **20**. We had originally intended to concentrate on compound **14**, but early in the program it was learned that Dr. John Fisher of NWC was pursuing the synthesis of DNDFP, (**14**), by essentially the same routes outlined by Dr. Rodney Willer while he was at NWC. In order to avoid any unnecessary duplication of effort, all work on the synthesis of DNDFP was discontinued at Morton Thiokol/Elkton.

The proposed synthesis of DNDFA is summarized in Scheme 4. The literature preparation of 4,4'-diamino-3,3'-bifurazan was repeated.[8] The cyclization of **21** to **15** has not been accomplished despite numerous attempts. The principal problem is that **21** is insoluble in water, the most common solvent for such reactions. The reaction of **21** with acetic anhydride has also been examined. Surprisingly, it is not acetylated by prolonged treatment with hot acetic anhydride; this may also be due to the low solubility of **21**. The alternate synthesis of **15** by the nitration of **21** to 4,4'-dinitramino-3,3'-bifurazan and cyclization of it to **15** was not examined because the program was shortened.



Scheme 4. Proposed Synthesis of DNDFA



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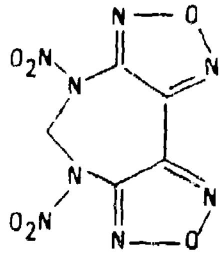
I_{SP} = 273 (PREDICTED)



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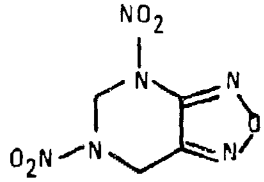

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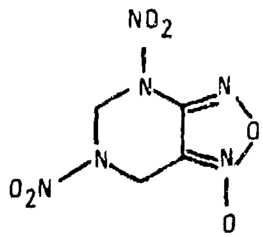
(DNFPY)



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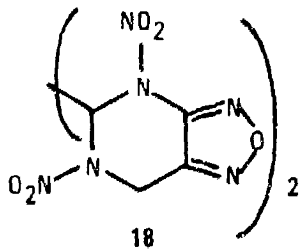
(DNFPY-O)



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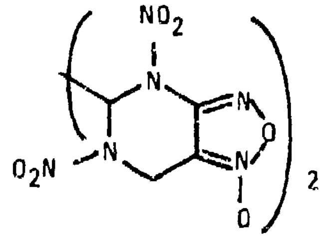
$(DNFPY)_2$



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$(DNFPY\text{-}O)_2$

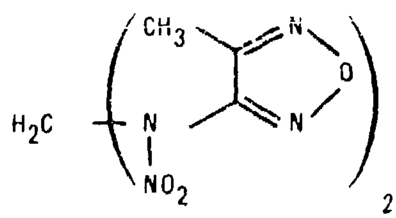

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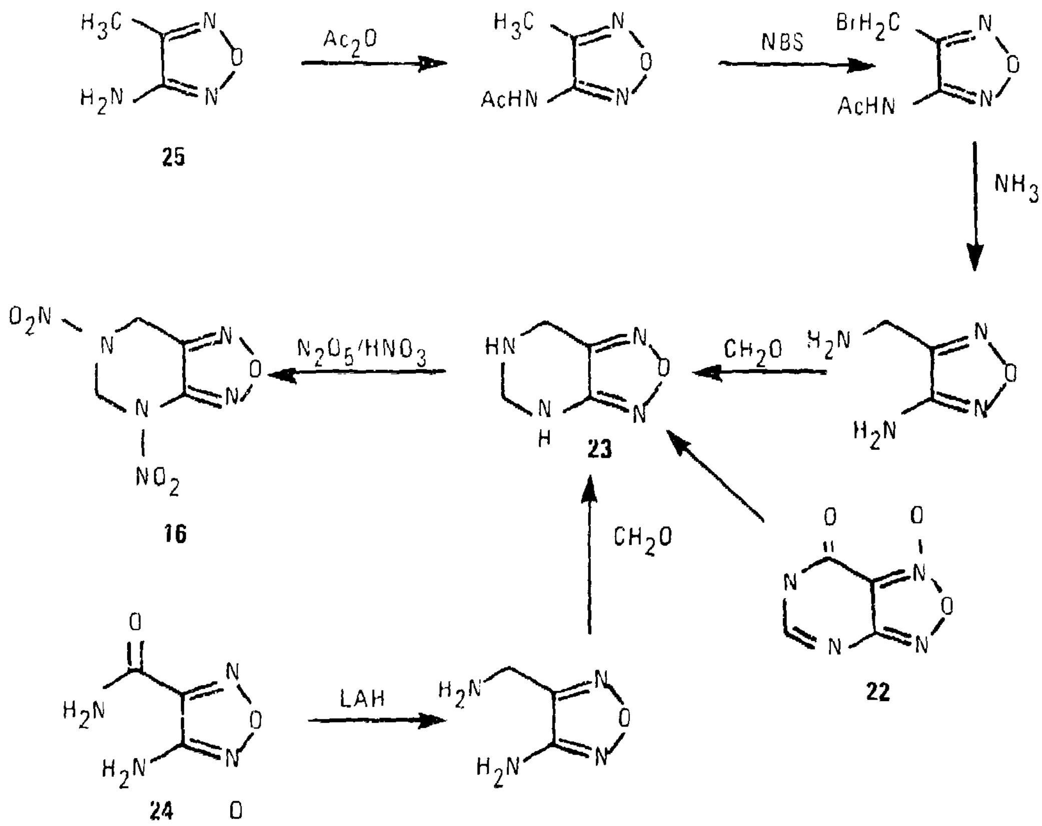
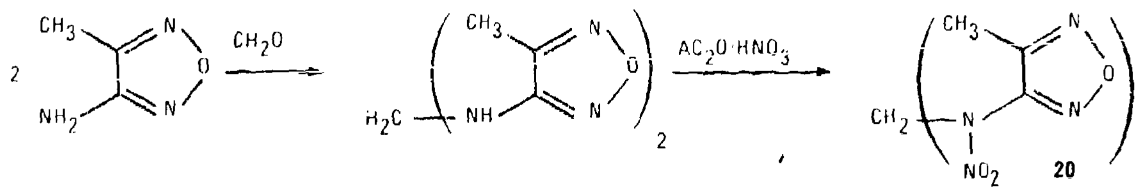
Figure 3. Target Furazan and Furoxan Molecules

The proposed synthetic routes to DNFPY, **16**, are shown in Scheme 5. The preparation of **22** was accomplished by a literature procedure.[13] An attempted direct reduction of **22** to **23** using LAH produced no isolatable products. However, a strong green color (possibly a nitroso compound) was produced during the reduction. The hydrolysis of **22** to **24** and reduction of **24** with $NaBH_4$ should be examined. The reduction of **22** using milder reducing reagents such as $NaBH_4$ should also be investigated.



Scheme 5. Proposed Routes to DNFPY

3-amino-4-methyl furazan (AMF), **25**, was synthesized by the base promoted dehydration of methyl amino glyoxime. This is a new synthetic procedure for this compound. The AMF was acetylated to the 3-acetamido-4-methyl furazan but no further work on the alternate route to DNFPY was conducted. AMF readily condenses with formaldehylde to give 3,3' methylene bis (3-amino-4-methylfurazan) and this can be nitrated by acetic anhydride/nitric acid to give the 3,3' methylene bis(3-nitramino 4-methylfurazan), **20**, (see Scheme 6).



Scheme 6. Synthesis of 3,3'-Methylene bis (3-nitramino-4-methylfurazan)

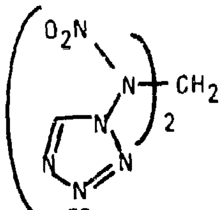
3.3 Synthesis and Chemistry of Tetrazolo-Fused Nitramines

3.3.1 Synthesis of Tetrazolo-Fused Nitramines. Figure 4 shows the target molecules in the tetrazolo-fused nitramine class of compounds. Efforts in this area have been concentrated on the synthesis of three compounds, methylene bis (1-nitraminotetrazole), **26,** 5-nitro-5,6-dihydro-7H-imidazolo [1,2-d]tetrazole, **27**, and 6,9-dinitro-6,7,8,9-tetrahydro-1H-triazolo [1,5-b] -1,2,4-triazine, **28.**

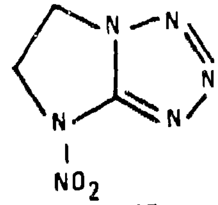
The synthesis of **26** is summarized in Scheme 7. The literature preparation of 1-aminotetrazole was successfully repeated.[14] A crystalline product from the reaction of 1-AT with formaldehyde has been isolated in low yield. This compound, m.p. 116.7-122.4^{o}C has a elemental analysis, IR, and ^{1} H NMR consistent with the desired methylene bis-(1-aminotetrazole). Insufficient material was isolated to investigate its nitration.

Compound **27** has been synthesized by the nitration of 5,6-dihydro-7H-imidazolo [1, 2-d] tetrazole, **31**, as summarized in Scheme 8. The infrared spectrum of **27** (see Figure 4) clearly establishes that it has the tetrazole structure and not the azido-azomethine structure.

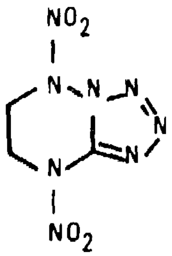
Compound **27** has the unusual property that it decomposes without going through a melt phase as shown by its DSC curve (see Figure 5). Heats of formation of **27** and **33** were measured to be +90 and+61 kcal/mole respectively. Based on its measured heat of formation, compound **27** has an I_{sp} (1000-14.7) of 238 sec. Further investigation of this compound at Morton Thiokol/Elkton as a gas generator ingredient and as a combustion rate modifier is planned.



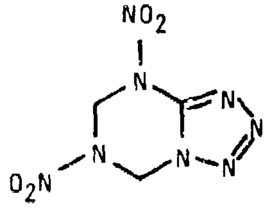
26



27



28



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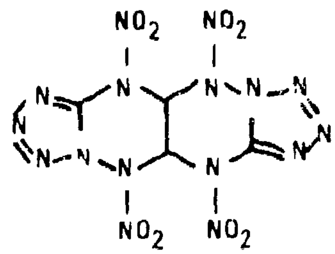
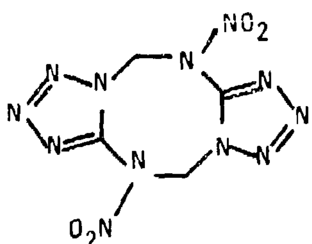
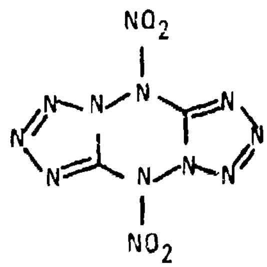


30

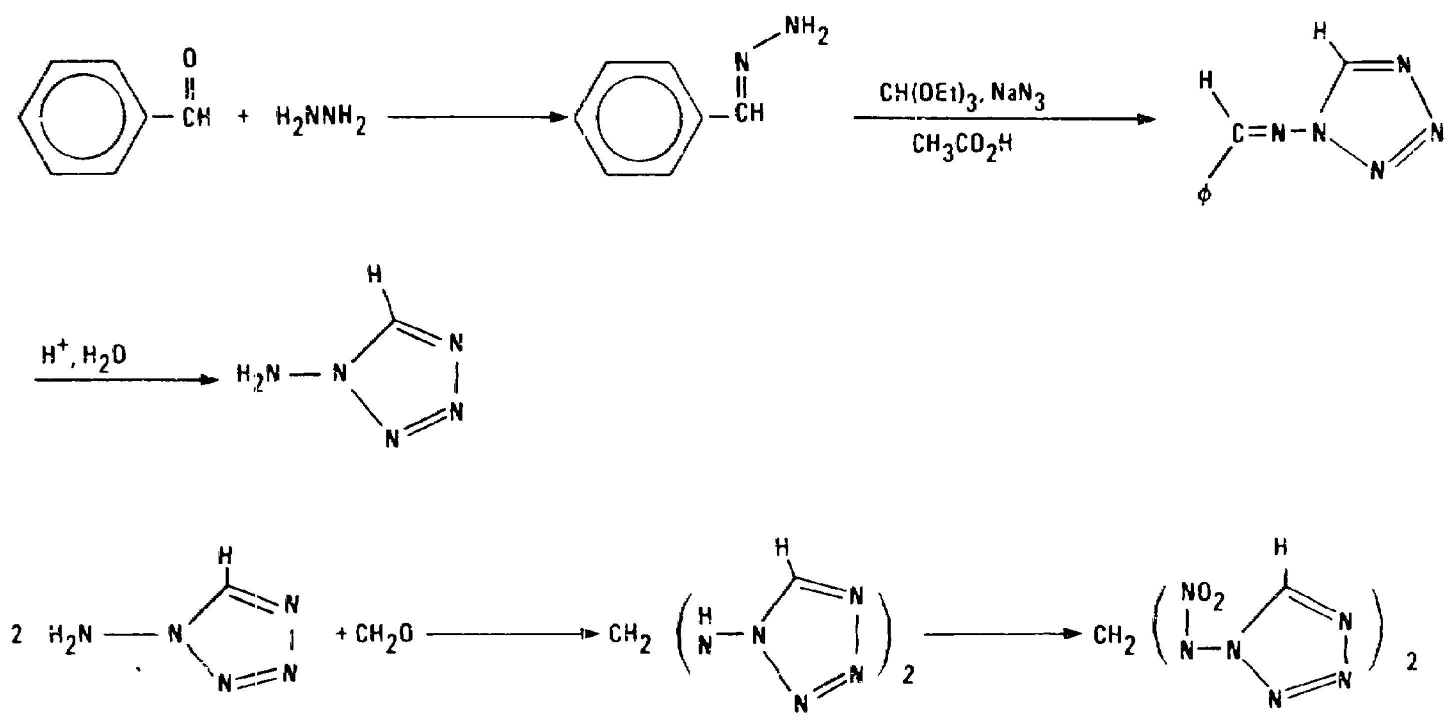


31

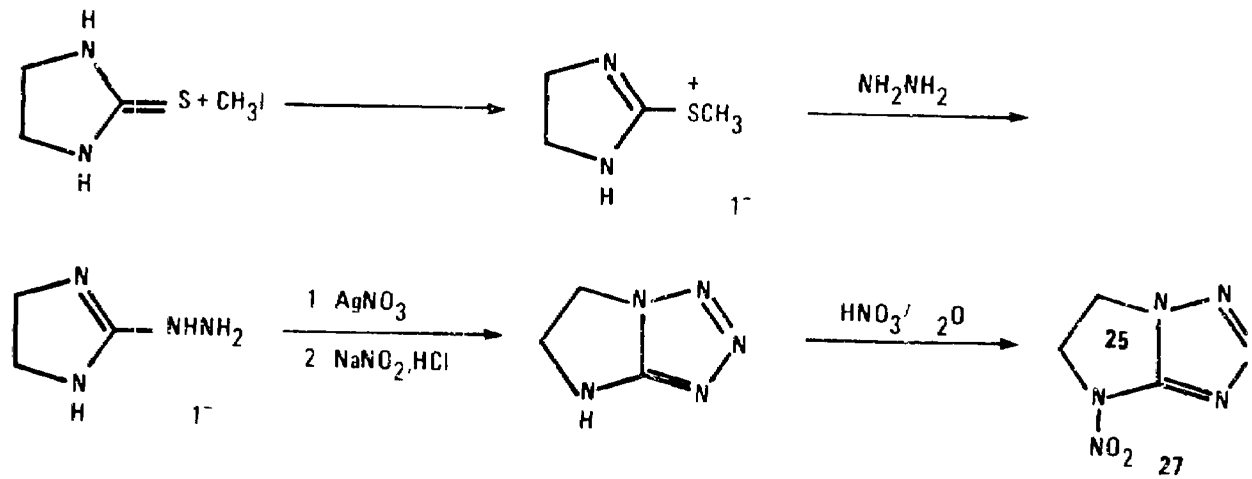


32

Figure 4. Target Tetrazolo-fused Nitramines



Scheme 7. Proposed Synthesis of Methylene Bis (1-Nitramino Tetrazole)



Scheme 8. Synthesis of 5-Nitro-5,6-Dihydro-7H-Imidazolo[1,2-d] Tetrazole

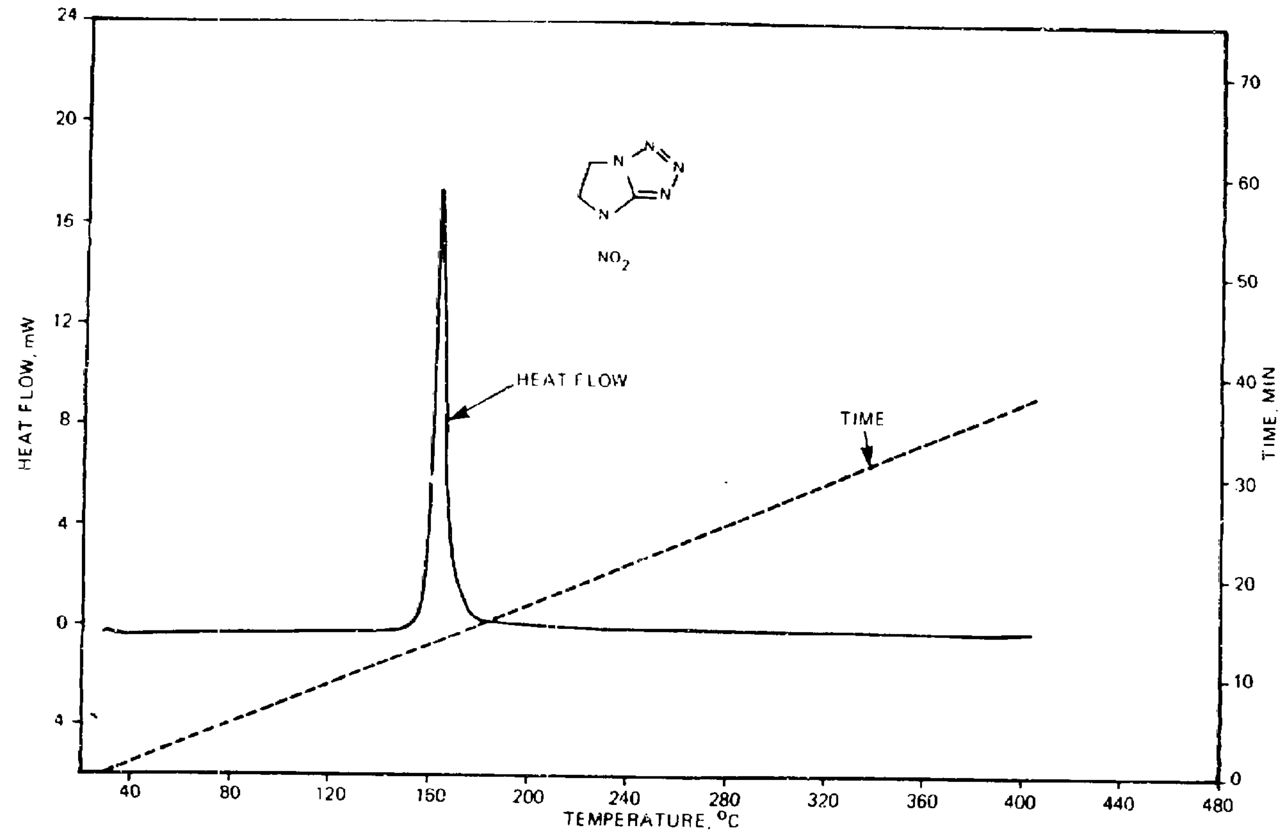
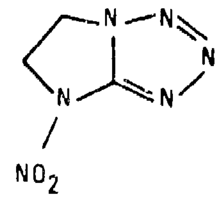


Figure 5. DSC Trace of 5-Nitro-5,6-Dihydro-7H-Imidazolo[1,2-D] Tetrazole

The crystal and molecular structure of **27** was solved by Drs. Clifford George and Richard Gilardi of the Naval Research Laboratory. Figure 6 presents a drawing of the molecule. Following is a summary of the physical and chemical properties of **27** (NDIT) which have been determined.



NDIT
27

Density (g/cc)	1.685 (x-ray) (1.622 predicted)
ΔH_f	+90 kcal/mole (measured)
M.p.	150°C (decomposition)
I_{sp}	238 sec
Detonation pressure	252 Kbar
Detonation velocity	7.692 m/sec

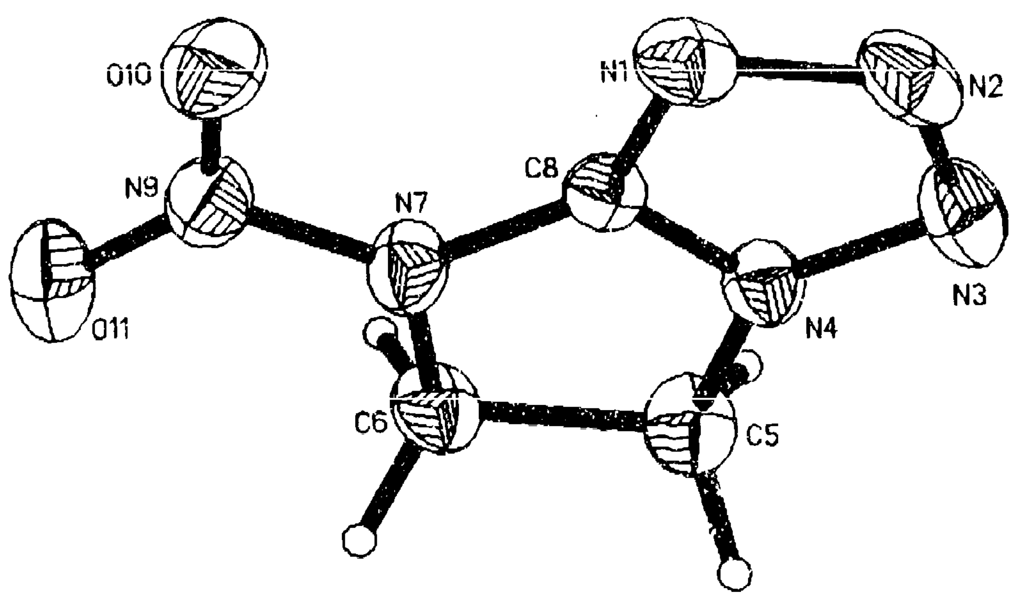
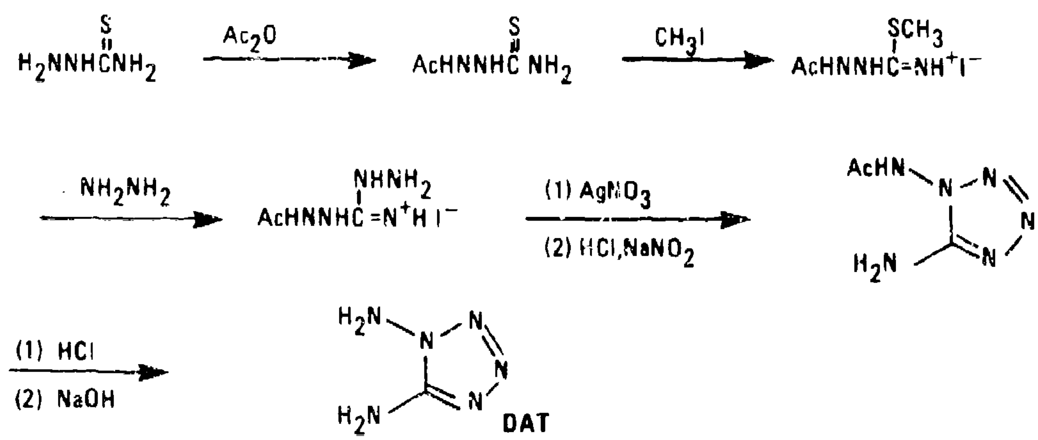
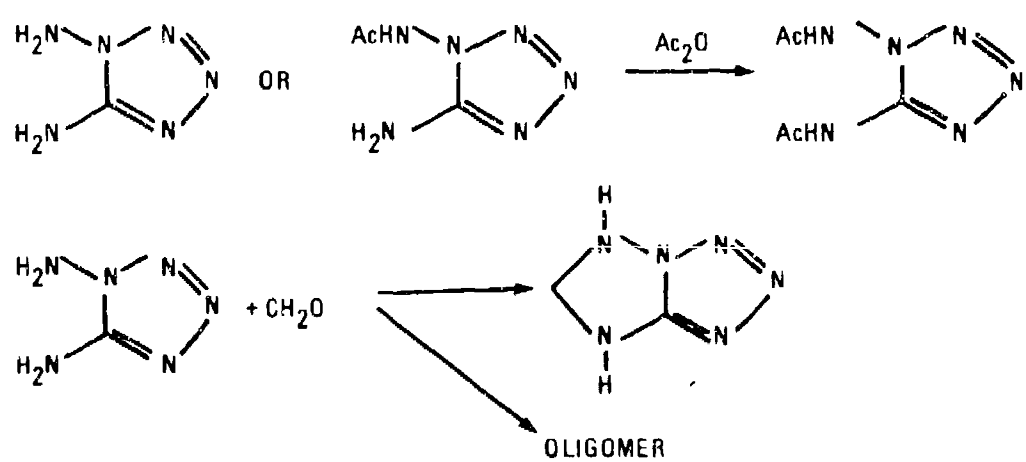


Figure 6. Molecular Structure of NDIT

Attention was then directed to synthesis of molecules derived from 1,5-diaminotetrazole. During the summer of 1985, Dr. Ron Henry of NWC provided an unpublished procedure for making 1,5-diaminotetrazole (DAT) which is outlined below in Scheme 9. Approximately 10g of DAT was synthesized using this procedure, and its reaction with acetic anhydride and formaldehyde was examined.



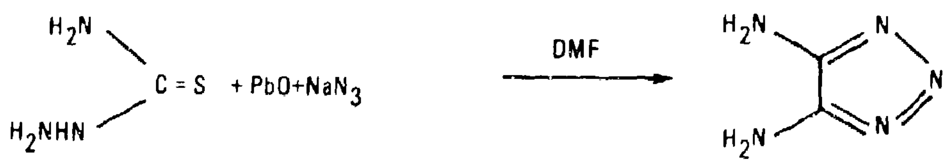
Scheme 9. Synthesis of 1,5-Diaminotetrazole



Scheme 10. Reactions of DAT

Both DAT and 1-acetamido-5-aminotetrazole can be acetylated to 1,5-diacetamidotetrazole with acetic anhydride and this compound is reasonably stable while melting with decomposition at approximately 200°C. This indicates that the analogous dinitramine, 1,5-dinitraminotetrazole, may also be stable. Similar to 3,4-diaminofurazan (DAF),[5] DAT forms an oligomer with formaldehyde instead of forming the bicyclic system. However, the product appears to have a lower molecular weight than the DAF-formaldehyde product.

An alternate synthesis of 1,5-diaminotetrazole (DAT) was found in the recent Russian literature (see Scheme 11). This simple procedure allowed approximately 1 lb of DAT to be synthesized. This increased amount of DAT greatly facilitated the exploration of its chemistry. The reaction of DAT with glyoxal and substituted glyoxal was carefully examined. As summarized in Scheme 12, the reaction of DAT hydrochloride with glyoxal, pyruvic aldehyde and biacetyl produces the tetrazolo-as-triazine (**33**, a, b, c) as the major or sole product when a 1:1 stoichiometry is used. With pyruvic aldehyde (methyl glyoxal) a mixture of two isomers is obtained. The tetracyclo products (**34** a, b) are obtained when a 2:1 stoichiometry is used with glyoxal or pyruvic aldehyde. It was found that the tetrazolo-as-triazines (**33**a, b, c) can be reduced to the dihydro derivatives (**35** a, b, c) by catalytic hydrogenation. The tetrahydro derivatives (**36** a, b, c) are obtained by sodium borohydride reduction. These are summarized in Scheme 13. The tetrahydro compound, **36** a, can be easily nitrated to the dinitro compound, **28**, using acetic anhydride/100% nitric acid. This was one of the target molecules of this subtask. The dihydro compound **35** a is nitrated under similar conditions to a mono-nitro compound **37**. It is not clear at this time whether nitrogen 6 or 9 is nitrated.



Scheme 11. Alternate Synthesis of DAT

The crystal and molecular structure of compound **28** were solved by Professor Reingold of the University of Delaware. It has $P2_1/c$ space group with a = 9.160 (3), b = 6.911 (3), c = 12.728 (4) Å, β = 90.15 (2), V = 805.7 (3) Å, Z = 4, Dx = 1.781 gm/cm^3 at 294K. A drawing of the molecule is given in Figure 7. As can be seen, there is considerable distortion in the molecules. Professor T. Brill of the University of Delaware will be studying the high rate thermolysis of the compound. The compound melts with decomposition at 103-104°C.

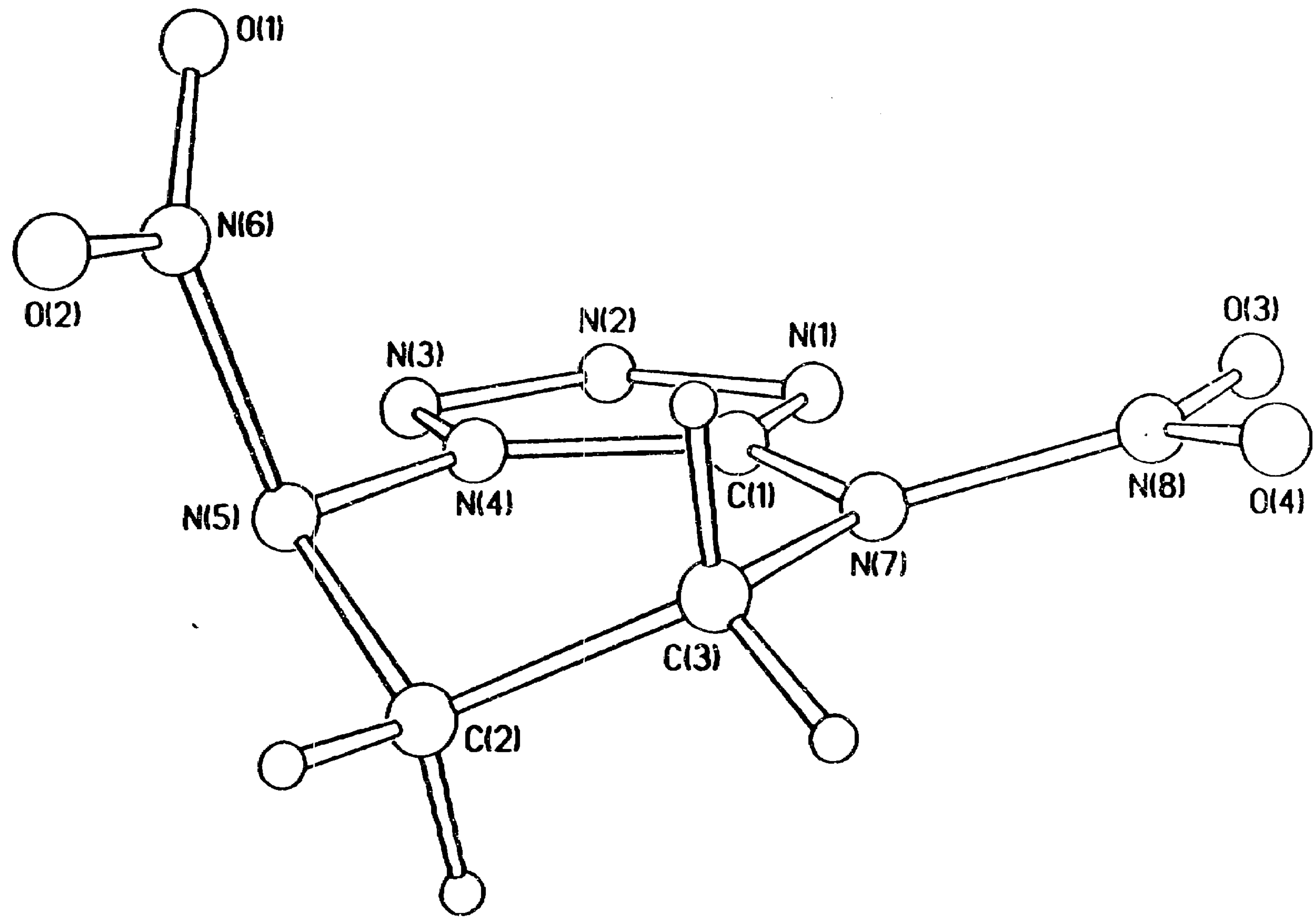
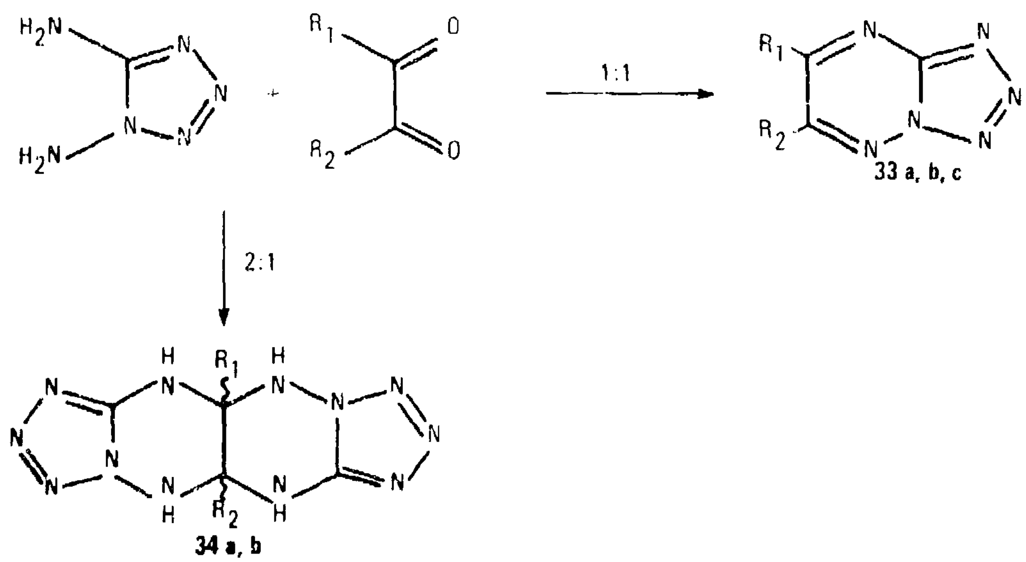
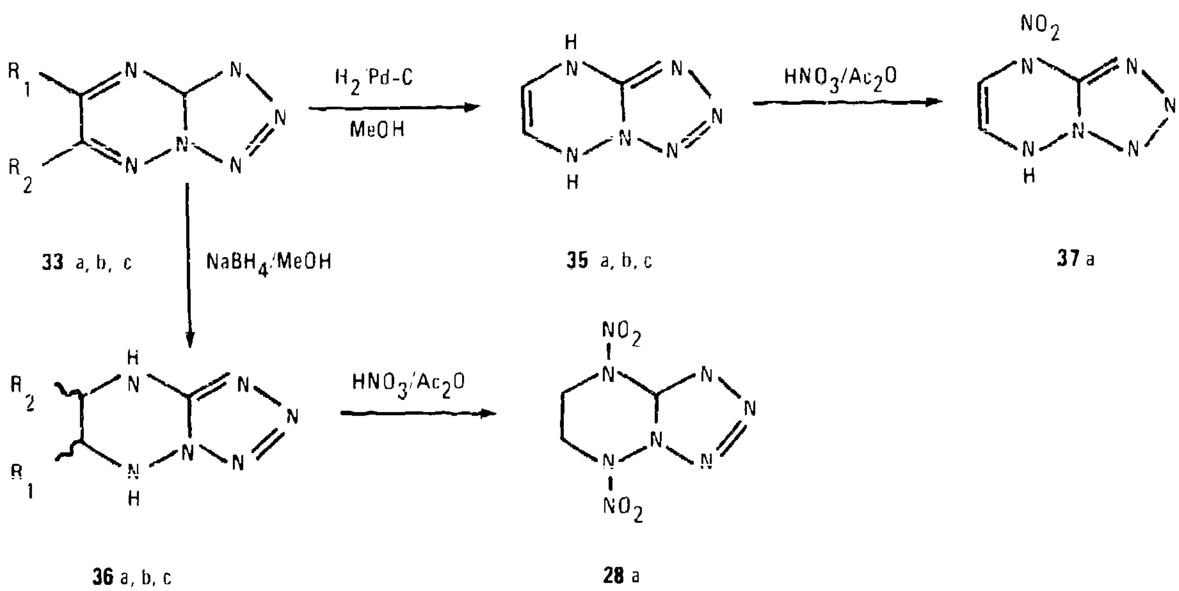


Figure 7. Molecular Structure of Dinitrotetrahydrotetrazolotriazene



Scheme 12. Chemistry of 1,5-diaminotetrazole (DAT) with Glyoxals



Scheme 13. Chemistry of Tetrazolo 1,5-b -1,2,4-Triazine

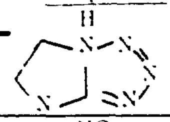
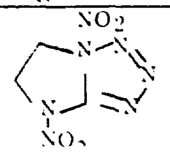
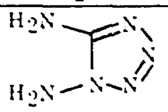
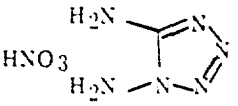
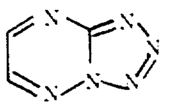
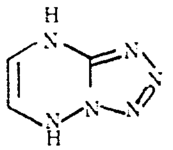
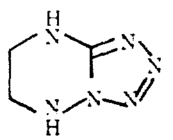
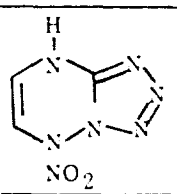
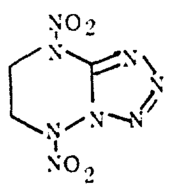
3.3.2 Chemistry of Tetrazolo Fused Compounds. We have also examined the heats of formation of these compounds. In Table 3, the heats of combustion and heats of formation for several of the new tetrazolo compounds synthesized under this program are summarized. These data are in excellent agreement with some previous data on the heats of combustion of tetrazole compounds by W. S. McEwan and M. W. Riggs[18]. A comparison of these data indicates that a 1-amino group on tetrazole contributes +25 kcal mole to the heat of formation.

3.4 Internal Plasticizers and Energetic Internal Plasticizers

Little work was accomplished on this task because reliable methods to cure ethylene glycol malonate prepolymer into gumstocks without using a plasticizer could not be developed.

TABLE 3. Measured Heats of Combustion of Tetrazole Compounds and Their Calculated Heats of Formation

SA21735

Compound	Molecular Formula	MW (g/mole)	H_c (cal/g)	H_f (kcal/mole)
	$C_3H_5N_5$	111.1	4628 ± 6	+61.1 ± 08
	$C_3H_4N_6O_2$	156.1	3262 ± 1	-90.29 ± 0.03
	CH_4N_6	100.1	3051 ± 6	+74.6 ± 0.6
	$CH_5N_7O_3$	163.1	1724 ± 7	+16.1 ± 1.1
	$C_3H_2N_6$	122.1	3926 ± 5	+128.8 ± 0.6
	$C_3H_4N_6$	124.1	4180 ± 26	99.9 ± 3.2
	$C_3H_6N_6$	126.1	4419 ± 8	+70.0 ± 1.0
	$C_3H_2N_8O_4$	214.1	TBD	TBD
	$C_3H_4N_8O_4$	216.1	2512 ± 8	+124.0 ± 2.0

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4.0 EXPERIMENTAL

3-Amino-4-Methyl-Furazan (AMF)

In a 1000-ml glass liner was placed 58.5 g (0.5 mole) of amino methyl glyoxime, 20 g (0.5 mole) of sodium hydroxide, and 100 ml of water. This was heated to 160°C for one hour in a medium pressure Parr reactor. The pressure reached a maximum of 150 psi. The reactor was cooled, opened, and the crude product collected. It was recrystallized from water to give 30.5 g (0.30 mole, 60%) of pure 3-amino-4-methyl furazan, m.p. 72-74°C. (lit[19] 72-73°C).

3,3'-Methylene bis (3-Amino-4-Methyl Furazan)

A solution of 4.0 g (40 mmoles) of AMF and 1.6 g of 37% formaldehyde in 50 ml of water was prepared. This was heated to reflux with stirring and one drop of conc. HCl was added. The product precipitated almost immediately. After 5 minutes, it was collected and washed with a small amount of water. The yield of product, m.p. 196-198°C, was 4.1 g (0.19 moles, 94%). Anal. calcd for $C_7H_{10}N_6O_2$: C, 40.00; H, 4.80; N, 39.97. Found: C, 00.00; H, 0.00; N, 00.00.

IR (KBr): 3350(s), 1611(s), 1563(s), 1394(m), 1241(m), 1121 (w), 1063 (w) cm^{-1}.. ^1H NMR (DMSO-d_6) δ = 2.15 (s, 6H), 4.65 (t, J = 6Hz, 2H) 7.25 (t, J = 6 Hz, exchanges) ppm.

3,3'-Methylene bis (3 Nitramino-4-Methyl Furazan)

A solution of 5 g of acetic anhydride and 5 g 100% nitric acid was prepared in the usual fashion. This was maintained at 0°C and 2.1 g (10 mmoles of 3,3'-methylene bis 3-amino-4-methyl furazan) was added in small portions over 10 minutes. The solution was stirred for 30 minutes at room temperature, then quenched on 50-g ice. The product was extracted into methylene chloride (3 x 25 ml), dried, filtered and the solvent removed at reduced pressure to give the crude product as a viscous liquid which slowly crystallized. The crystals were slurried in cold methanol and collected and washed with a small amount of cold methanol. The product melts at 87-90°C. Anal. Calcd for $C_7H_8N_8O_6$; C, 28.01; H, 2.69; N, 37.32. Found: C, 0.00; H, 0.00; N, 0.00.

IR(KBr) 3050(w), 1595(s), 1507(w) 1442(w), 1426(w), 1403(w), 1390(w), 1282(s), 1093(m), 1037(w), 898(w), 768(w), 752(w), 734(w), 672(w), 632(w) cm^{-1}.

^1H NMR ($CDCl_3$) δ = 2.35 ppm (s, 6H), 6.60 ppm (s, 2H) ppm.

1,4-Dinitro-2,5-diketopiperazine

In a 100-ml two-neck r.b. flask equipped with a magnetic stirrer, thermometer, and droppi ; funnel were placed 10 ml of acetic anhydride. This was cooled to 0°C by means of an a salt-ice bath and 10 ml of 100% nitric acid was added dropwise over 10 minutes. The solution was stirred for 20 minutes, then 5.52 g (0.05 moles) of 2,3-diketopiperazine were added in small portions over 10 minutes. The solution was stirred for 1 hour, then quenched on ice. The product was collected and washed with a small amount of methanol. The driver product weighed 9.8 g (0.048 moles, 96%). The compound decomposes at 158-162°C.

IR (KBr): 2999 (w), 2950 (w), 2850 (w), 1732 (s), 1590 (s), 1437 (w), 1384 (w), 1276 (m), 1258 (m), 1158 (m), 1023 (m), 978 (w), 943 (w), 808 (w), 794 (W) cm^{-1}.

NMR (CD_3COCD_3) δ =

5,6-Dihydro-1H-imidazolo [1,2-d] tetrazole

This compound was prepared by the procedure of Finnegan, Henry, and Lieber.[15]

7-Nitro-5,6-Dihydro-1H imidazolo [1,2-d] Tetrazole, 27

In a 25 ml ratio r.b. flask equipped with a magnetic stirring bar were placed 10 g of acetic anhydride. This was cooled to 0°C (salt-ice bath), and 10 g 100% nitric acid were added in drops for 10 minutes. This nitrating solution was stirred for 20 minutes; then 5.55 g of 5,6-dihydro-1H imidazolo [1,2-d] tetrazole (50 mmoles) were added in small portions for 10 minutes. The solution was stirred for 20 minutes, then quenched on 50 g of crushed ice. The crude product was collected, washed with water, and dried. The yield was 5.9 g of colorless crystals (37 mmoles; 75% yield). The compound decomposed at 155°C. Anal Calcd. for $C_3H_4N_6O_2$: C, 23.09; H, 2.58; N, 53.83. Found: C, 00.00; H, 0.00; N, 00.00.

IR(KBr): 3010 (w), 1591 (vs), 1550 (m), 1512 (w), 1471 (w), 1334 (vs), 1300 (s), 1266 (sh), 1235 (w), 1205 (w), 1185 (w), 800 (w), 765 (w), 747 (w), 715 (w), 683 (w) cm^{-1}.

NMR (CD_3SOCD_3) δ = 4.75 (m, 2H, H_5), 5.05 (m, 2H, H_6) ppm.

1,5-Diaminotetrazole (DAT)

This compound was synthesized by two procedures, both of which start with semicarbazide. The first, an unpublished procedure by Dr. Ronald Henry,[16] is a six-step procedure summarized in Scheme 9. The second is a one-step procedure by Gaponik[17] and Karavai which is summarized in Scheme 11. The second procedure is clearly the preferred one for the synthesis of DAT and has been successfully scaled to the 1.0 mole scale.

1-Aminotetrazole

This compound was synthesized by the procedure of Gaponik and Karavai.[14]

1-H-Tetrazolo [1,5-b]-1,2,4-triazine, 33a.

In a 500 ml erlenmeyer flask were placed 18.0 g (0.125 mole) of 40% glyoxal, 100 ml distilled water, and 10 g concentrated hydrochloric acid. This solution was warmed to 60^{o}C and stirred while 10 g (0.1 mole) of 1,5-diaminotetrazole was added in small portions over 5 minutes. The product started to precipitate after about one minute. The mixture was stirred for 15 additional minutes, then cooled to below 5^{o}C in an ice/water bath. The crude product was collected and washed with 50 ml distilled water. The moist product was dissolved in 300 ml hot water, filtered to remove a small amount of insoluble by-product, and slowly cooled to below 5^{o}C. The product was collected and dried. The yield of purified product m.p. 188^{o}C was 8.5 to 9.0 g (0.07 to 0.073 mole, 70-73%). Anal. Calcd for $C_3H_2N_6$: C, 29.51; H, 1.65:N. 68.83. Found: C, 29.22; H, 1.90; N, 68.78.

IR (KBr): 3097(m), 3050(w), 1584(s), 1538(s), 1496(s), 1341(s), 1307(s), 1284(m), 1242(s), 1085(s), 1013(m), 983(s), 934(s), 874(s), 780(m), 761(m), cm^{-1}.

^{1}H NMR (DMSO-d_6) δ = 9.1 (d, 1H, J = 2Hz), 9.20 (d, 1H, J = 2Hz) ppm.

Mixture of 7- and 8-Methyl-1-H tetrazolo[1,5-b]-1,2,4-triazine, 33b

In a similar fashion, pyruvic aldehyde and 1,5-DAT were condensed to give an approximate 50/50 mixture of 7- and 8-methyl-1-H tetrazolo[1,5-b]-1,2,4-triazine. The mixture has a melting point of 120-130^{o}C. Anal. Calcd. for $C_4H_4N_6$: C, 35.30; H, 2.96; N, 61.73. Found: C, 35.10; H, 2.84; N, 62.00.

^{2}H NMR (DMSO-d_6) δ = 2.70 (s, 3H), 2.73 (s, 3H), 8.97 (s, 1H), 9.12 (s, 1H) ppm.

7,8-Dimethyl-1-H-tetrazolo[1,5-b]-1,2,4-triazine, 33c

In a similar fashion biacetyl and 1,5-DAT were condensed to give 7,8-dimethyl-1-H-tetrazolo[1,5-b]-1,2,4-triazine. The compound melted at 133-137^{o}C. Anal. Calcd for $C_5H_6N_6$: C, 40.00; H, 4.03; N, 55.96. Found: C, 00.00; H, 0.00; N, 00.00.

IR (KBr): 3123 (w), 3023 (w), 2950 (w), 2900 (w), 1688 (w), 1652 (w), 1590 (m), 1530 (W), 1499 (m), 1440 (m), 1395 (s), 1290 (sh), 1284 (m), 1094 (m), 1001 (m), 985 (m), 773 (W), 687 (w) cm^{-1}.

^{1}H NMR (DMSO-d_6) δ = 2.80 (s, 3H), 2.83 (s, 3H) ppm.

Dihydro-1H-Tetrazolo[1,5-b]-1,2,4-triazine, 35a

In a clean 500-ml Parr hydrogenation bottle were placed 2.0 g of 1-H tetrazolo 1,5-b -1,2,4-triazine, 250 ml methanol and 1 g 5% Pd/C. The mixture was stirred for 15 minutes to dissolve the starting material, then it was hydrogenated at 60 psi for one hour. A stream of nitrogen is run through the solution for a few minutes. Then it is heated to reflux and filtered through a fiberglass filter to remove the catalyst. The solvent was removed at reduced pressure to give 1.4 g (70% yield) of crude product. The crude product was recrystallized from DMSO/H_2O to give the product as light red needles, m.p. 159-161°C. Anal. Calcd for $C_3H_4N_6$: C, 29.04; H, 3.25: N, 67.71. Found: C, 28.96; H, 3.55; N, 67.60.

IR (KBr): 3400(b), 3271(s), 3104(m), 2972(w), 2930(w), 2908(w), 1652(s), 1629(s), 1490(m), 1451(w), 1397(w), 1337(m), 1289(w), 1255(w), 1208(w), 1099(m), 1051(w), 996(m), 903(w), 758(w), 724(m), 669(m), 632(w), 627(m) cm^{-1}.

^1H NMR (DMSO-d_6) δ = 4.20 (M, 2H), 7.4 (t, 1H, J = 2Hz), 7.85 (bs, 1H) ppm.

6,7,8,9-Tetrahydro-1H-Tetrazolo[1,5-b]-1,2,4-triazine, 36a

In a 1500-ml erlenmeyer flask were placed 12.2 g (0.1 mole) of **33c** and 500 ml methanol. This slurry was stirred and the temperature adjusted to 10°C by means of an ice water bath. Sodium borohydride (5.0 g, 0.13 mole) was added in one portion. The starting material dissolved immediately upon adding the sodium borohydride. The mixture was stirred for 30 minutes, then the solvent was removed at reduced pressure to give a yellow solid. This was dissolved in 50 ml of water and the water was removed at reduced pressure to give a white solid. This was dissolved in 20 ml of hot water, filtered, and cooled. The product crystallized and was collected and washed with a small amount of cold water. After drying, the product (m.p 145-147°C) weighed 12.3 g (0.096 mole, 96%). Anal. calcd for $C_3H_6N_6$: C, 28.57; H, 4.80; N, 66.63. Found: C, 28.54; H, 4.89; N, 66.50.

IR (KBr), 3294(b), 3226(s), 2991(w), 2933(m), 2882(m), 1630(vs), 1520(m), 1475(m), 1446(w), 1346(m), 1304(m), 1220(w), 1130(m), 1099(m), 1063(m), 1020(m), 982(w), 962(m), 918(w), 763(w), 732(w), 704(w), 666(w), cm^{-1}.

^1H NMR (DMSO-d_6) δ = 3.30 (m, 4H), 7.0 (t, 1H, J = 6Hz) 7.7 (bs, 1H) ppm.

Mixture of 7- and 8-Methyl-6,7,8,9-Tetrahydro-1,-H-Tetrazolo [1,5b] -1,2,4-triazine, 36b

In a similar fashion the mixture of 7- and 8-methyl-1H-tetrazolo[1,5b]-1,2,4-triazine was reduced to a mixture of 6,7,8,9-tetrahydro derivatives. Upon prolonged standing one isomer crystallized. It has a m.p. of 140-141°C. Anal. calcd. for $C_4H_8N_6$ C, 34.29; H, 5.76; N, 59.96. Found: C, 00.00; H, 0.00; N, 0.00.

IR (KBr): 3205 (vs), 2982 (m), 2941 (m), 2867 (m), 1622 (s), 1525 (w), 1450 (w), 1388 (w), 1361 (w), 1262 (m), 1125 (w), 1101 (m), 981 (m), 935 (m), 909 (w), 900 (w)cm^{-1}.

^1H NMR $(CD_3)_2CO$ δ = 1.25 (d, J = 6 Hz, 3H), 3.90-3.80 (m, 3H), 6.2 (d, J = 8 Hz, 1H, exchanges), 6.8 (bs, 1H) ppm.

6,7,8,9-Tetrahydro-7,8-Dimethyl-1-H-Tetrazolo[1,5b]-1,2,4-triazine, 36c

Similar reduction of 7,8-dimethyl-1-H-tetrazolo [1,5b] -1,2,4-triazine with sodium borohydride gave the tetrahydro derivative as a 2:1 mixture of two stereoisomers, m.p. 127-133°C. Anal. calcd. for $C_5H_{10}N_6$: C, 38.96; H, 6.54; N, 54.58. Found: C, 00.00; H, 0.00; N, 00.00.

In a 100 ml r.b. flask was placed 4.0 g (40 M moles) of 1,5-diaminotetrazole, 2.90 g of 40% glyoxal (20 M moles) 1 drop concentrated HCl, 20 ml distilled water. This mixture was stirred, heated to reflux for 30 minutes, and cooled; and the product was collected and dried. The yield of crude product was 3.1 g (13 mmoles, 70%). The compound did not melt but decomposed above 200°C. Anal. calculated for $C_4H_6N_{12}$: C, 21.63; H, 2.72; N, 75.65. Found: C, 00.00; H, 0.00; N, 00.00.

IR (KBr), 3305(s), 3136(s), 1651(vs), 1598(m), 1461(m), 1326(w), 1260(w), 1109(m), 1069(m), 989(w), 947(w) cm^{-1}.

6(or 9)-Nitro-6,9-Dihydro-1,H-Tetrazol[1,5b]-1,2,4-Triazine, 37

Nitration of 0.62 g (5 mmoles) of 35a using acetic anhydride (4 g) and nitric acid (8.0 g) by the usual procedure gave 0.82 g (4.7 mmoles, 95%) of the mono-nitro derivative. The compound decomposed when recrystallized. The m.p. of the crude product is 124-126°C (dece). Anal. Calcd for $C_3H_3N_7O_2$: C, 21.31; H, 1.79; N, 57.97. Found: C, 21.43; H, 1.87; N, 57.69.

IR (KBr) 3412(b), 3075(w), 2959(w), 2932(w), 1596(s), 1552(m), 1441(w), 1423(w), 1354(m), 1318(s), 1269(s), 1213(w), 1151(m), 1110(w), 1010(w), 954(w), 775(w), 750(w), 700(w), cm^{-1}

^1H NMR $((CD_3)_2CO)$ δ = 5.50 (d, J = 2Hz, 2H), 8.2 (t, J = 2Hz, 1H) ppm

6,9-Dinitro-6,7,8,9-Tetrahydro-1-H-tetrazolo[1,5-b]-1,2,4-triazine, 28

In a 25-ml r.b. flask equipped with a magnetic stirring bar were placed 8.0 ml of 100% nitric acid. This was cooled to 0°C and 4 ml acetic anhydride was added dropwise over 2 minutes. This mixture was stirred for 10 minutes. The temperature was lowered to -20°C and then 1.26 g (10.0 mmoles) of **36**a were added in small portions over 10 minutes. The mixture was stirred at 0°C for 10 minutes, then quenched on ice. After the ice had melted, the crude product was isolated by filtration and dried in a vacuum. After drying the product weighed 2.1 g (9.5 mmoles, 95%). The product was recrystallized by dissolving it in acetone at room temperature and precipitating it out by adding

water. The purified product has a m.p. of 102-104°C (dec). Anal. calculated for $C_3H_4N_8O_4$: C, 16.68; H, 1.87; N, 51.84. Found C, 17.03: H, 1.74: N, 51.75.

IR (KBr): 3100(w), 2850(w), 1638(s), 1606(s), 1563(w), 1435(w), 1369(w), 1345(w), 1306(s), 1267(s), 1132(m), 1042(w), 1012(w), 832(m), 778(w), 746(w), 713(w) cm^{-1}.

'H NMR (CD_3COCD_3) δ = 4.60 (t, 2H, J = 5.5Hz), 5.00 (t, 2H, J = 5.5 Hz) ppm.

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6.0 PUBLICATIONS

During the contract, two manuscripts describing work conducted on the program were published. One manuscript was accepted for publication and two manuscripts are in preparation. These are listed below:

"Synthesis and Chemistry of Some Furazano- and Furoxano [3,4-b] Piperazines," by R. L. Willer and D. W. Moore, appeared in J. Org, Chem., 50, 5123 (1985).

"1,3-Dinitroso-, 1-Nitroso-, 3-Nitro-, and 1,3-Dinitro-1, 3-Diazacycloalkanes. A Multi-Nuclear NMR Study," by R. L. Willer and D. W. Moore, accepted for publication in "Magnetic Resonance in Chemistry." Should appear in late 1987.

"Synthesis of Polycyclic Polynitramines and Nitramine substituted Heterocycles," R. L. Willer, 1986 ADPA Symposium on Compatability of Plastics and other materials with Explosives, Propellants, and Pyrotechnics and Processing of Propellants, Explosives, and Ingredients, Oct 27-29, 1986, Long Beach, CA

"Synthesis and Chemistry of Some Tetrazolo [1,5-b] -1,2,4-Triazines," R. L. Willer and R. A. Henry, manuscript in preparation for submission to J. Org. Chem.

"Heats of Formation of Some α-Dioximes, Furazans, and Furoxans," by R. L. Willer, J. C. Hill, and R. A. Biddle. Manuscript in preparation to be submitted to either J. Org. Chem. or J. Phy. Chem.